Radiocarbon dating of lime mortars

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Radiocarbon and radiocarbon dating method

Radiocarbon dating is the measurement of the age of a sample based on the comparison of the radioactive carbon ^{14}C content in it at the time of dating with the amount of ^{14}C initially contained.[1]

Radioactive carbon ^{14}C (or, more simply, radiocarbon) is one of the three principal isotopes of carbon, together with ^{13}C and ^{12}C (an isotope is a variant of a specific chemical element with the same number of protons of the most diffused specie but a different number of neutrons). Compared to the ^{13}C and ^{12}C stable isotopes, radiocarbon is unstable due to the excess of neutrons in its nucleus (8 instead of the 6 contained in ^{12}C and the 7 in ^{13}C). Its instability results in a decay to nitrogen-14 (^{14}N) that produces emission of an electron known to physicists as a weak β particle. This decay is described on the right hand side of Figure 1.

In nuclear physics and nuclear chemistry, the time required on a probabilistic base for half of an unstable isotope to undergo radioactive decay is called the half-life. The half-life of radiocarbon is 5,730 years. This means that every 5,730 years about half of the

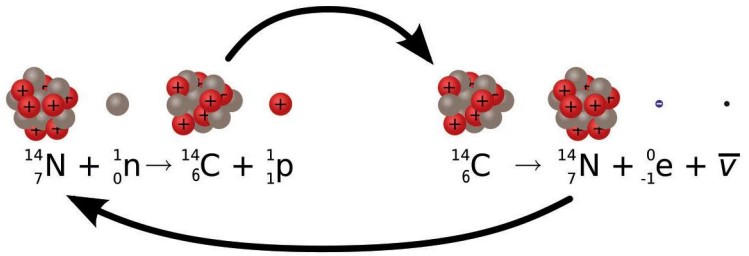


Fig. 1 Formation (left-hand side) and decay (right-hand side) of radiocarbon. Modified version of an image taken from Wikipedia[2] and licensed under the Creative Common Attribution-Share Alike 3.0 Unported license.

initial ^{14}C contained in a specimen decays into ^{14}N. As a consequence, in 11,460 years the amount of ^{14}C contained in a specimen is a quarter of the initial amount, and so on.

Radiocarbon is produced in the high atmosphere and, in particular, in the upper layers of the troposphere and stratosphere by the effect of cosmic rays on the ^{14}N contained in it. When the cosmic rays enter the atmosphere, they undergo various transformations, including the production of neutrons. These neutrons (^{1}n) take part in the reaction that converts the ^{14}N to ^{14}C, as described on the left-hand side of Figure 1.

Compared to the other carbon isotopes, the amount of radiocarbon produced by the cosmic rays is relatively small. It has been calculated that 98.89 per cent of the total carbon existing in the earth's atmosphere is ^{12}C, 1.11 per cent is ^{13}C, and only 0.0000000001 per cent is ^{14}C. This means that only one ^{14}C atom exists in nature for every trillion ^{12}C atoms.

As well as the other carbon atoms, the ^{14}C formed in the atmosphere is rapidly oxidised by oxygen, forming CO_2. Through this molecule it easily enters into the normal chemical processes active on earth. For instance, plants continuously absorb atmospheric CO_2 through photosynthesis fixing the radiocarbon in their cells. Animals feed on plants and absorb the radiocarbon. Humans eat animal meat, in turn absorbing the radioactive carbon.

Despite the natural decay of radiocarbon that would lead to a reduction in the total amount of ^{14}C contained in living organisms, continuous absorption of CO_2 from the atmosphere allows them constantly to maintain the same level of ^{14}C in their structure (equal to the amount of ^{14}C contained in the atmosphere). At their death, though, the assimilation process stops and the radioactive decay loss is no longer compensated by the intake of food. As a consequence, following its death, a living organism starts to lose radiocarbon atoms.

Because the ^{14}C decays at a known rate, it is possible to know the age of death of an organism by measuring its ^{14}C content and comparing this with the initial content (supposed as corresponding to the amount of ^{14}C contained in the atmosphere at the time when the organism lived, which, as an initial approximation, can be considered constant over the time). This method is called radiocarbon dating, or simply carbon dating. The basic principle underlying it was first suggested by Professor Willar Libby (1908–1980) who, in the mid-1940s, realised that the decay of radioactive carbon could lead to a method for dating organic matter. In 1960 he received the Nobel Prize for his work in developing radiocarbon dating.

Technique for measuring radiocarbon

At the beginning, the only way to measure the amount of ^{14}C contained in a sample was to detect the radioactive decay of individual carbon atoms (i.e. the electrons emitted). The technique was known as beta-counting because what was detected was the number of β particles (i.e. the electrons) emitted by the decaying of ^{14}C.

In the late 1970s, however, an alternative technique became available, thanks to the introduction of accelerator mass spectrometry (AMS). AMS allows the number of ^{14}C and ^{12}C atoms in a sample to be determined on the basis of their mass instead of the basis of the particles emitted (Figure 2). The method allows the dating of samples containing only a few milligrams of carbon, such as individual seeds, but despite this sensitivity it is not yet possible to date materials older than about 50,000 years (approximately nine half-lives of ^{14}C). The amount of radiocarbon still contained in the samples after such a long time is too small to be reliably measured with currently available instruments.[4] In order to be measured with AMS, the carbon contained in the sample has to be turned into graphite.

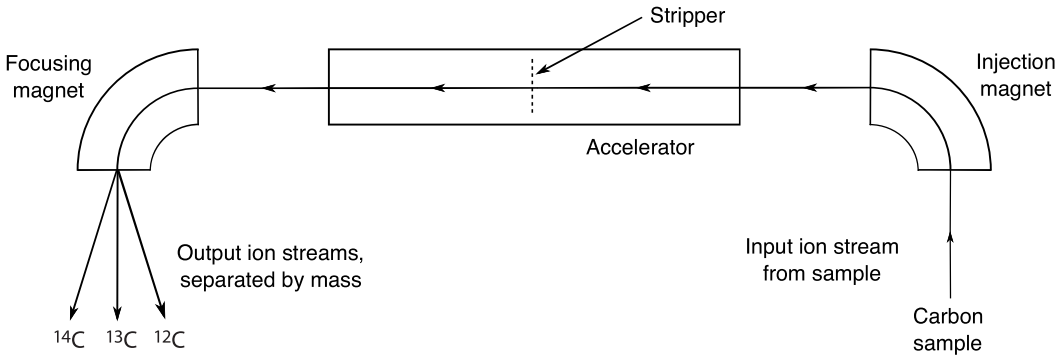


Fig. 2 Simplified layout of an accelerator mass spectrometer. Image taken from Wikipedia[3] and licensed under the Creative Commons Attribution-Share Alike 3.0 Unported license.

Calibration curve

In the description of the radiocarbon dating method proposed above, it is assumed that the concentration of ^{14}C atoms in a living sample is known and equal to the concentration of the ^{14}C atoms contained in the atmosphere. In this description it is also assumed that the number of ^{14}C atoms contained in the atmosphere has been constant over time, so that measuring the number of ^{14}C atoms in the sample at a specific time easily allows calculation of the sample's age. Unfortunately, the level of ^{14}C in the biosphere has varied significantly over time and, consequently, the results obtainable with this radiocarbon dating method have to be corrected using calibration curves. A number of sources affected, and can still now affect, the radiocarbon content in the atmosphere. These include, for instance, natural atmospheric variations, the impact of climatic cycles, the effects of human activity, and volcanoes. All the calibration curves currently available consider the effects of all these sources.[5]

Basic principles of the radiocarbon dating of lime mortars

A number of studies carried out over the last forty years describe the application of the radiocarbon dating method to lime mixtures such as mortars, plasters, and renders.[6–13] The basic principles of this particular application of carbon dating were first suggested in a short paper published in *Nature* in 1964 by Labeyrie and Delibrias.[14] Here are some of their words:

> Old mortars are ordinarily composed of about 80 per cent by weight of coarse sand particles embedded in a matrix of calcium carbonate needles. Therefore, 1 kg of mortar contains about 90 g of carbon dioxide, which has been incorporated through a process of diffusion from the ambient atmosphere when the mortar has been prepared. The carbon dioxide capture process lasts about one week after the moment when lime and sand have been mixed with water. From this moment the proportion of carbon-14 in the carbon of the calcium carbonate needles must decrease in the same way as it does after death in plants or animals, and therefore buildings constructed with these mortars can possibly be dated by the usual carbon-14 method.

To understand the basic principle of this application it is necessary first to consider the lime-manufacturing process.

Traditional lime is produced from limestones with different levels of purity but essentially composed of $CaCO_3$ of geological origin. The limestone is burnt at about 900°C in special kilns to produce gaseous CO_2 and a solid phase essentially composed of calcium oxide (CaO) or quicklime.[15–17] Equation 1 shows the chemistry of this thermal treatment and highlights that the solid phase produced at its end is free of carbon.

$$(1)\quad CaCO_{3(s)} \xrightarrow{heat\ (900^{o}C)} CaO_{(s)} + CO_{2(g)}$$

Subsequently, the quicklime undergoes a slaking process where it combines with water. The resulting exothermic reaction forms $Ca(OH)_2$ according to Equation 2, which shows that no carbon is added to the lime during this process.

$$(2)\quad CaO + H_2O \longrightarrow Ca\,(OH)_2 + heat$$

In the past this process was almost exclusively carried out using an excess of water, resulting in the formation of lime putty, one of the most widely used inorganic binders for construction. Plasters, renders, mortars, and other architectural features were (and still are) formed by mixing the lime with sand, and in some cases with other additives.

When in place, the major part of the $Ca(OH)_2$ within the mixtures hardens by carbonation, resulting in the formation of new $CaCO_3$ with acquisition of atmospheric carbon. This process is described in Equations 3–8, where the dissolution process of atmospheric CO_2 (Equations 3–6) in water is emphasised according to the model proposed by Morse and Mackenzie:[18]

$$(3)\quad C^{*}O_{2(g)} \rightleftharpoons C^{*}O_{2(aq)}$$

$$(4)\quad C^{*}O_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2C^{*}O_{3(aq)}$$

$$(5)\quad H_2C^{*}O_{3(aq)} \rightleftharpoons HC^{*}O^{-}_{3(aq)} + H^{+}_{(aq)}$$

$$(6)\quad HC^{*}O^{-}_{3(aq)} \rightleftharpoons CO^{*2-}_{3(aq)} + H^{+}_{(aq)}$$

$$(7)\quad Ca\,(OH)_{2(s)} + H_2O_{(l)} \rightleftharpoons Ca^{2+}_{(aq)} + 2(OH)^{-}_{(aq)} + H_2O_{(l)}$$

$$(8)\quad Ca^{2+}_{(aq)} + C^{*}O^{2-}_{3(aq)} + H_2O_{(l)} \rightleftharpoons CaC^{*}O_{3(s)} + H_2O_{(l)}$$

In this system, Equation 3 represents the dissolution in water of atmospheric CO_2 containing $1x10^{-12}$ parts of ^{14}C (represented by the C*). Equations 4–6 show how the radiocarbon dissolved in water can form the carbonate ion necessary to the carbonation reaction without (theoretically) being subjected to any change. In the meantime, lime particles dissolve in water, forming calcium and hydroxyl ions (Equation 7). Equation 8 represents precipitation of a $CaCO_3$ solid phase that forms by reaction between Ca^{2+} and CO_3^{2-} ions containing radiocarbon.

Overall, these equations highlight the fact that, together with the other carbon atoms, ^{14}C atoms contained in the atmosphere are trapped in the structure of $CaCO_3$ at the time of hardening so that the concentration of ^{14}C in the hardened lime reflects the concentration of atmospheric radiocarbon at the time of hardening.

At the end of the carbonation process, the carbon (and with it also the radiocarbon) is fixed in the structure of a mineral (the $CaCO_3$) with low solubility, and therefore it can hardly be replaced by new radioactive atoms. This means that at the end of carbonation the acquisition process of ^{14}C stops, so that the radioactive decay loss cannot be compensated by the intake of new carbon. As a consequence, following the end of carbonation, a lime-based mixture starts to lose radiocarbon atoms in the same way as any living organism at the time of its death and, therefore, the material can be dated with the radiocarbon method.

From an archaeological point of view, the most interesting point of this process is that the fixation of radiocarbon within the $CaCO_3$ structure (i.e. the hardening process of lime) occurs approximately at the time of construction, which is the information very often sought by archaeologists when buildings are studied. This means that, potentially, radiocarbon dating of mortars can be the most reliable technique for dating old structures. Other techniques currently used to date historic mortars are in fact based on the use of the organic matter contained within the mixture. Unfortunately, however, very often the relation between this matter and the mortars is not known, so that the results obtainable must be carefully evaluated.

Drawbacks and limitations

Contamination from ^{14}C-dead

Despite the fact that the radiocarbon dating of mortars is very simple in principle, several studies have highlighted various practical challenges and factors that must be considered.[19]

These arise mainly from the fact that it is currently impossible to separate the $CaCO_3$ produced by the hardening process of lime from the $CaCO_3$ contained in other sources within the mortars.

Sample contamination with carbonaceous substances can be due to several factors, such as the presence of incompletely burnt pieces of limestone (i.e. pieces of the same stone used to produce the lime that have not been completely decomposed during the thermal process) or aggregates of fossil origin, including limestone sand.

Carbonate rocks, in fact, are mainly made of $CaCO_3$ that, at the beginning of the sedimentary process, contained all the carbon isotopes contained in the earth's atmosphere at the time of the precipitation. However, in contrast to the carbon contained in the lime mixtures which have a lifetime shorter than the radiocarbon's half-life, the $CaCO_3$ of geological origin comes from times far earlier than that, equivalent to the decay time of radiocarbon. This means that the carbon contained in carbonate rocks is ^{14}C-dead and, consequently, any piece of carbonate rock contained in a mortar sample (such as grains of carbonate sand or pieces of under-burned limestone) can affect the result of radiocarbon dating by diluting the ^{14}C concentration of lime.

The presence of aggregate grains or pieces of stone would not be a problem if a technique for separating them from the lime was available. Unfortunately, even if under the microscope it is possible to distinguish between the lime and the aggregate, from a practical point of view their separation is almost impossible when both are made of $CaCO_3$.

The only case when this separation is practicable is when the aggregate is made of quartz. In contrast to $CaCO_3$, quartz does not dissolve in hydrochloric acid (HCl) or phosphoric acid (H_3PO_4) and, consequently, dissolving a lime-based mortar containing quartz aggregate in acid allows capture of carbon (and with it the radiocarbon) as gaseous CO_2, as shown in Equation 9.

$$(9)\quad CaCO_{3(s)} + 2HCl_{(aq)} \longrightarrow CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

The CO_2 released by acid dissolution can be easily transformed in graphite using a reactor vessel (similar to a test tube), where the gas is reacted with iron powder and hydrogen gas. The graphite produced in this process can be used in the AMS as a source of pure carbon for the carbon dating. However, this case is not frequent and, besides, there still remains the problem of under-burned pieces of stone that can be contained in the mixture and behave in a manner similar to the binder under acid attack.

Dissolution and re-precipitation of $CaCO_3$

The previous statement about the immutability of carbon contained in the $CaCO_3$ phases precipitated during the hardening process of lime has exceptions. Calcium carbonate is, in fact, soluble in water (even though its solubility is quite low) and this means that sometimes the carbonated lime contained in building materials can be affected by a process of dissolution and re-precipitation. This process leads to an exchange of carbon atoms that has a negative effect on the radiocarbon dating results.[20]

Typical water sources that can produce this process are: rain (mainly affecting renders but also mortars, if the building is in a state of disrepair), groundwater aquifers (mainly affecting foundations and ground-floor flooring), and rising damp (mainly affecting plasters, renders, and mortars).

The dissolution process of $CaCO_3$ is described in Equation 10, which shows that, once in solution, the Ca^{2+} is free from the previous bonds with the carbonate ion and thus can react with new CO_3^{2-} ions in the same manner as described in Equation 8, to produce new $CaCO_3$. However, in this case the carbon available in solution can be made of both atoms from the dissolved $CaCO_3$ and atoms from the atmosphere at the time of dissolution (that can have a different ^{14}C to ^{12}C ratio compared to the atmosphere at the time of hardening of the lime).

$$(10)\quad CaCO_{3(s)} + CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons Ca^{2+}_{(aq)} + 2HCO^{-}_{3(aq)}$$

It is for this reason that results of the radiocarbon dating of lime mortars containing even a small amount of re-precipitated $CaCO_3$ (i.e. secondary $CaCO_3$) can be different from the results of the radiocarbon dating of the same lime containing only primary $CaCO_3$ (i.e. precipitated at the time of the hardening process).

Delay in the hardening process of lime

Labeyrie's statement (quoted above) that the CO_2-capture process of lime lasts about a week is not proven. Carbonation is a very slow process that depends on several factors such as temperature, moisture content, and pore structure of the mortars in which the lime is used. Since all these factors are quite changeable from site to site, and within the same site, the hardening time of lime mortars can be quite variable.

Carbonation can stop if the environment becomes too dry or too wet, or if the CO_2 access is inhibited.[21,22] Under these conditions carbonation can only start again following a change in the water content of the mortar and/or CO_2 access (e.g. when cracks caused by carbonation shrinkage form). Scientific investigations of old buildings have already highlighted that the inner part of thick walls, such as old city walls, can still contain $Ca(OH)_2$, even centuries after their construction.[23,24] On the contrary, superficial layers such as plasters and renders tend to carbonate quickly because of the more favourable conditions for carbonation (e.g. easier CO_2 access, water evaporation, and condensation).

A possible delay in carbonation affects the results of any related radiocarbon dating. This means that results of radiocarbon dating of historic mortars depend not only on the purity of the samples but also on the depth of the sample within the analysed structure. For this reason, superficial samples are more desirable than deep samples.

Techniques for the radiocarbon dating of lime mortars

Over time, improved techniques for the acid dissolution of lime mortars have been developed to separate the lime from the aggregate. However, despite all efforts, there still remain some uncertainties in the results of the radiocarbon dating obtained from these techniques.[25–27]

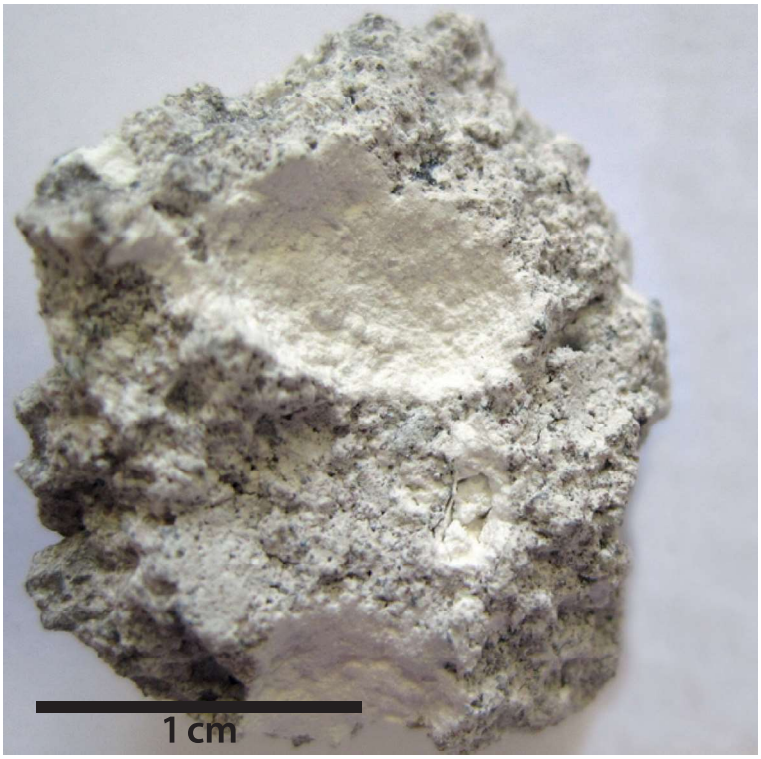
The techniques are based on complex processes that include mechanical and chemical separation.[e.g.28,29] In one of the most advanced techniques currently used, the mortar is initially gently crushed with a pestle and mortar and the resulting material is sieved using increasingly fine mesh widths (typically 46–75 microns). Following the mechanical separation, the resulting particles are analysed to verify the presence of any contaminants.

If the sample does not contain contaminants, chemical separation is obtained by pouring phosphoric acid over the powdered sample under vacuum. Theoretically, since carbonated lime dissolves more easily than limestone,[30] it is possible to collect the CO_2 produced by the dissolution of the binder without contamination from the CO_2 produced by dissolution of the $CaCO_3$ of geological origin. The dissolution process, in fact, starts out quite violently, at the beginning mainly liberating the CO_2 from the carbonated lime. Successively, the reaction slows down and the dissolution of geological carbonate begins. Unfortunately, despite the correctness of the theoretical principle, from a practical point of view it is impossible to recognise precisely when the dissolution of the binder ends and the dissolution of the aggregate begins.

For this reason, the gas produced by acid dissolution is collected in glass vials in a number of successive fractions (for example, five) that are dated separately in order to create a profile age of the sample. The profile age is then studied in order to evaluate the age of the fraction that best represents the actual age of the mortar (generally the first one[31]).

Another similar technique introduces a different physical pre-treatment of the samples, which includes an ultrasonic attack in liquid phase. This allows isolation from bulk mortars of a suspension of carbonated lime which is supposed to be free from contaminants.[32]

More recently, however, a technique that provides a completely different approach to the sample selection and preparation has been proposed. The technique is based on the use of lumps of pure lime instead of the generic pieces of mortar used in the other techniques. These lumps are thought to originate from imperfect mixing of lime and sand during the building process and are quite common in mixtures predating mechanical mixing. The basic principle is that, since these lumps contain the same lime used in other parts



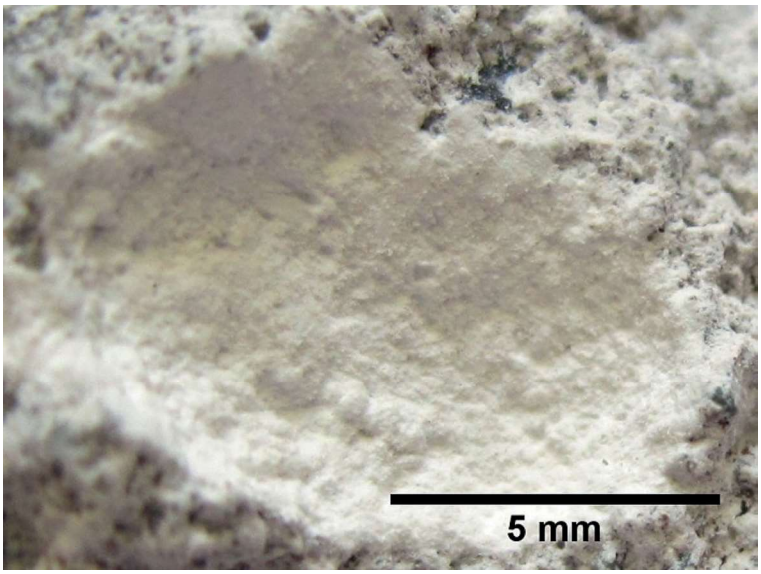


Fig. 3 Pure lime lump in a specimen of air-lime mortar; below, detail of the same lime lump.

of the mixtures but are naturally free of contaminants, they can be successfully used for the radiocarbon dating of mortars.

The pure-lime-lumps technique

It is known that during the older lime-mortar-manufacturing process, some lumps of lime, not mixed with sand, could remain embedded within the mortars.[33–36] At that time, once the quicklime was completely transformed into $Ca(OH)_2$, the lime putty was filtered and stored in pits dug in the ground or immediately mixed with sand and other materials to produce the desired mixtures.[37–40] The slaking process was assisted by continuous manual mixing, carried out with specific tools. During this process, some small lumps of lime could remain compact and fail to mix intimately with the sand grains, even though they were able to combine with the atmospheric CO_2 in the same manner as the remaining matrix.

According to some research, the composition of these lumps is similar to that of the surrounding matrix,[41–43] with differences only in the micro-morphology. In particular, the matrix of the lumps appears to be more compact and with smaller pores compared with the surrounding matrix. Besides, in many cases the crystal growth is smaller in the lumps than in the matrix.[44,45]

Unfortunately, these lumps of pure lime are not the only lumps contained in old mortars. The internal structure of historic lime mixtures has, in fact, been found to contain at least five different types of lump, each of which can be recognised individually. These comprise:

- under-burned pieces of limestone;[46–48]
- over-burned pieces of limestone;[49–52]
- pieces of burned limestone containing high concentrations of silica (these arise when the stone used for the lime production contains a high quantity of impurities);[53,54]
- a concretion of recarbonated lime;
- lumps of pure $CaCO_3$ produced by the carbonation of lime.[55–61]

Among these types only the lumps belonging to the latter group are suitable for radiocarbon dating. Over-burned pieces of lime may, in fact, have been subject to a delayed carbonation caused by the sintered CaO crystals contained in them that are less reactive with water and, consequently, slower to react with CO_2.[62] Unburned pieces of limestone still contain CO_2 of geological origin (that, as previously discussed, can affect the radiocarbon dating result), while calcium contained inside the lumps of silica is mainly bonded to the silicon rather than to the CO_2.[63] Problems connected with concretions have been discussed previously.

Lumps of pure lime are, however, easily recognisable as they have a white, rounded, and floury appearance (Figure 3). The surface hardness of these lumps is very low, making them extremely delicate to handle and easily damaged.

The minimum amount of $CaCO_3$ required for a meaningful analysis by AMS is 20 milligrams, which is a very small amount but very often comparable to the mass of a single lump. Besides, if a single lump does not contain sufficient material, multiple lumps from the same area (i.e. from the same stratigraphic unit) can be used for the radiocarbon dating.

Sample preparation

When a suitable lump is identified within the structure to be dated, the sample is carefully removed in order to prevent damage. Following on-site sampling and before treatment and analysis at the AMS laboratory, the sample is analysed under an optical stereo microscope to confirm the lump nature and mechanically remove particles of aggregate that may still be attached to the sample surface.

Observation under an optical microscope is important since very often it is difficult on site to distinguish lumps of incompletely burnt limestone or other types of lump from the pure lime lumps; under a magnifying glass, even at low magnification, it is possible to recognise the lumps of pure lime. At this stage, evaluation of the superficial hardness is a very useful method for distinguishing between the different types of lump. Even performing a crude test, by hand, using a needle point, allows different types of lump to be effectively distinguished.

Following successful identification, all pieces of sand still attached to the surface of the lumps are removed using tools such as scalpels or needles. In order to remove as many pieces of sand as possible, the work is usually carried out using a stereo microscope. Great care has to be taken in this phase as the lumps are very delicate and easily damaged.

At the AMS laboratory the lumps are processed using the standard treatment for carbonate. Upon arrival, the sample is usually treated with hydrogen peroxide (H_2O_2) to chemically remove the outside layer. Approximately half of the minimum amount of the pre-cleaned sample is dried in an oven, where it is again treated with H_2O_2 and converted to CO_2 using phosphoric acid (H_3PO_4). The CO_2 extracted from the sample is then reduced to graphite using hydrogen (H_2) in the presence of an iron-powder catalyst. The graphite is finally pressed into tablets which are used in the AMS for measurement of the carbon isotopic ratios.[64,65]

Applications of the pure-lime-lumps technique

In 2008 a detailed example of this sampling and dating method was presented during an international conference in Cyprus. This work involved the collection of two lime lumps from the apses of the medieval church of St Nicolò of Campodimonte (Camogli, Genoa, in Italy) and dating with the radiocarbon method. The results obtained were evaluated and compared with the radiocarbon dating of organic material collected in the same apses and with the results of other dating methods.[66]

Prior to this test, relatively few researchers had carried out radiocarbon dating of lime lumps in archaeological sites, the exceptions being N. Gallo, on the medieval castle of Aghinolfi (Massa Carrara, Italy)[67] and L. Fieni, on the basilica of St Lorenzo Maggiore in Milan (Italy).[68]

However, since 2008, additional tests have been carried out by the research group of the Institute for the History of Material Culture of Genoa (Italy).[e.g.69,70] To date, a total of 33 samples taken from 10 different archaeological sites were dated following the procedure described. In about 88 per cent of cases, results were found to be consistent with the respective archaeological framework and uncertainty in radiocarbon dating was often reduced by comparison with other archaeological information. In about 12 per cent of cases, however, the results were archaeologically meaningless and this suggests that the technique still needs to be improved.

The church of St Nicolò of Capodimonte

The church of St Nicolò of Capodimonte is a medieval church on the Portofino mountain with a crux commissa (T-shaped) plan (Figure 4). Recently, during some restoration works, a multidisciplinary approach was adopted to study its principal construction stages. The work included archaeological analysis of the walls, research on bibliographic sources, and radiocarbon dating of mortars. Archaeological evidence and

Fig. 4 Facade of the medieval church of St Nicolò of Capodimonte (Camogli, Genoa, Italy).

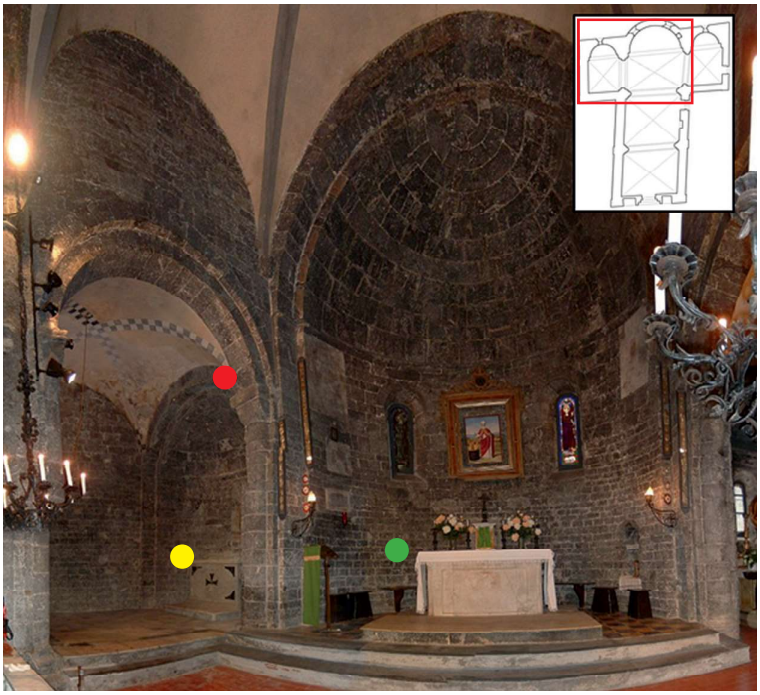


Fig. 5 Sampling points inside the church of St Nicolò of Capodimonte. The red mark indicates Sample 1, the yellow mark Sample 2, and the green mark Sample 3.

Sample no.	Laboratory no.	^{14}C age (BP)	Calibrated age (AD)	Probability (%)	Expected age (century)
1	LTL2133A	917±55	1010–1220	95,4	XII–XIII
2	LTL2978A	1005±45	890–920	2,7	XI
			960–1160	92,7	
3	LTL2132A	790±60	1040–1090	4,6	XIII–XIV
			1120–1300	90,8	

Table 1 Radiocarbon ages obtained for Samples 1 to 3.

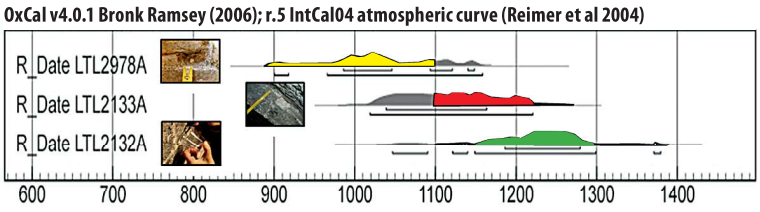


Fig. 6 Comparison of the calibrated data for St Nicolò of Capodimonte. The red colour indicates Sample 1, the yellow Sample 2, and the green Sample 3. Coloured areas in the calibrated curves show the most likely period of time for the single result after comparison with other dating methods.

bibliographic sources suggested that the church was originally built during the 11th century and underwent some major changes during the 12th and 13th centuries. Nevertheless, the lack of detailed documentation about the different construction phases suggested that results from a more direct and absolute dating method would be desirable.

Radiocarbon dating was applied to two lumps of pure lime and a sample of organic matter. Sampling of lumps was possible through the large mortar joints (>1 cm thickness) and within damaged areas of the masonry. Samples were taken at a depth of about 1–2 cm inside the wall to ensure an early carbonation of lime. The first sample (Sample 1 in Table 1 and the red mark in Figures 5 and 6) was removed from the wall next to the interior border of the apsidal basin, on the right-hand side of the transept. The second sample (Sample 2 in Table 1 and the yellow mark in Figures 5 and 6) was removed from the external face of a wall, under the same apsidal basin. The sample of organic matter (Sample 3 in Table 1 and the green mark in Figures 5 and 6) was removed from the internal face of the main apse. Although the stratigraphic position of the first two samples was clear (Sample 2 had to be older than Sample 1), the position of the third sample was not perfectly established, as it could have been a part of the mortar used for the construction of the wall, or a residual part of a more recent plaster applied on the interior face of the wall.

The samples were submitted for radiocarbon dating at the laboratory of the Centre for Dating and Diagnostics at the University of Salento (Lecce, Italy). At the laboratory, the lime lumps underwent the standard process used for carbonates, whereas the organic sample was treated using the acid-alkali-acid protocol.[71] Table 1 shows the radiocarbon ages of the three samples together with the calibrated and expected ages.

Sample 2 was dated between the end of the 10th century and the middle of the 12th century AD, Sample 1 between the 11th and the 12th centuries AD, and the sample of organic matter was dated to the last construction phase of the building within the 13th century AD.

Overall, these results show that the ages obtained are consistent with the results of stratigraphic analysis and with the information available on the history of the building. The archaeological analysis led, in fact, to the identification of three main building phases, all dated to the Middle Ages. Bibliographic sources reveal that the church existed as early as the 12th century, when two congregations of monks undertook work on the building, while the last documented construction phase was dated to the 13th century. Sample 2 was selected from structures of unknown age but stratigraphically older than the structures built during the 12th century, while Sample 1 was selected from structures archaeologically dated to the 12th century. Sample 3 (organic matter) was ascribed to the last construction phase of the building, dated to the 13th century on the basis of the typology of the wall and on the dimensions of stones.

Overall, the radiocarbon dating results confirmed the expected ages of the samples and their stratigraphic position.

Conclusions

Radiocarbon dating results obtained for the church of St Nicolò of Capodimonte provide only a very simple example of radiocarbon dating of lime mixtures. However, experience gained through this and other studies highlights the importance and future potential of this dating method for conservators and archaeologists. Radiocarbon dating of mortar is, in fact, still quite an unknown subject among most operators in the field of cultural heritage, but if future applications confirm the positive results, such as those obtained at St Nicolò of Capodimonte or at Alba cathedral (Alba, Italy[72]), it is clear that this dating method will have an important role in the conservation of historic buildings and in archaeology in the future.

The pure-lime-lumps technique is still under development, but it is already clear that, because of its simplicity, once fully developed it will be an important technique for the radiocarbon dating of lime mixtures. Furthermore, the results already achieved show that this technique will allow an important reduction in the cost of radiocarbon dating of mortars, since even a single lump produces reliable chronological information (whereas with the other techniques for a single chronological date point, several individual gas samples have to be collected and dated).

Success of the technique, however, will depend on the development of appropriate protocols for the removal and preparation of the sample and on the appropriate training of the operators who will apply the technique (potentially conservators and archaeologists). Knowledge of the chemical, physical, and mechanical processes involved in the carbonation reaction, for instance, are of fundamental importance in understanding and applying this technique. To date, the full potential is still to be discovered and more research is needed. Unknowns include, for instance, the dating of mixtures containing hydraulic lime, which account for a significant proportion of historic mortar.

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